Inorganica Chimica Acta

Contents lists available at ScienceDirect



journal homepage: www.elsevier.com/locate/ica

Research paper

A novel pyridine-containing half-salamo-based "on-off-on" fluorescent sensor for continuous detecting Cu^{2+} and S^{2-} , and its structural features of copper(II) complex

Wen-Ze Zhang, Ruo-Yu Li, Peng Li, Zhuang-Zhuang Chen, Wen-Kui Dong

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, PR China

ARTICLE INFO	A B S T R A C T
Keywords: Half-salamo-based probe Copper(II) complex Crystal structure Fluorescence recognition Continuous identification	A novel sensor PNS for the continuous recognition of Cu^{2+} and S^{2-} was synthesized, specifically recognizes Cu^{2+} in DMSO/H ₂ O (9:1 v/v) solution by fluorescence emission spectroscopy. The colour of the PNS solution changed from colourless to yellow when Cu^{2+} was added under the fluorescent lamp, and at excitation wavelengths of 301 and 365 nm, the violet fluorescence of the PNS solution was quenched. The PNS-Cu complex formed by the sensor PNS and Cu^{2+} can further identify S^{2-} in the fluorescence spectra. The LOD values of the two substances both Cu^{2+} and S^{2-} are 1.21×10^{-8} and 5.58×10^{-9} M. In addition, single crystals of the PNS-Cu complex were also obtained to verify the principle of this continuous identification process.

1. Introduction

Copper(II) ion is indispensible component human body [1], and is an essential trace element, it plays a critical role in the function of many cellular enzymes [2]. However, when excessive amounts of copper are consumed, it can cause acute copper toxicity, hepatoenteric degeneration, and intrahepatic cholestasis in children [3]. The detection of anions in the environment by efficient, simple, and inexpensive techniques has also been an area of extensive research in recent years [4]. As the simplest sulfide anion, sulfide ions are widely distributed in wastewater samples and in natural water samples [5]. High concentrations of sulfide ions, an important indicator of water contamination, and excessive concentrations can cause apoptosis, Alzheimer's disease, and cirrhosis of the liver [4e,5c]. Therefore, it is of great significance to develop a chemosensor to identify these two substances [5g,6].

Currently, salen-based ligands and their derivatives continue to play an important role in modern coordination chemistry due to their significant applications in the fields of luminescence properties [7], catalytic activities [8], electrochemistry [9], host–guest recognition [10], magnetic materials [11], supramolecular structures [12] and bioactivities [13], and are therefore of great research value. The introduction of oxygen atoms onto salen-based ligands leads to the production of salamo-based ligands [14] having a N₂O₂ coordination environment and a more stable molecular structure. When new substituents are introduced into the benzene rings of salamo-based ligands these changes lead to larger structural changes and new properties of their corresponding complexes [15]. Some salamo- and bis(salamo)based sensors for the recognition of different ions have been investigated in the past few years [16], the use of fluorescence as probes of halfsalamo-based compounds is rarely reported. Half-salamo-based ligands not only have the stabilities of the salamo- and bis(salamo)-based ligands, but also retain a phenolic oxygen atom, which results in the formation of a cavity of N₃O. In this paper, a newly-designed half-salamo-based sensor was synthesized, and which can continuously recognize copper(II) and sulfide ions. The PNS-Cu complex formed by sensor PNS and copper(II) ions can further recognize sulfide ions in solution. This half-salamo-based complex sensor is a new type of probe derived from half-salamo-based oxime-type sensor, which not only retains the stability of salamo-based sensor in aqueous solutions and increases the hydrophilicity of molecule, but also broadens the molecular construction of salamo-based sensor, which is important for improving the system for the detection of inorganic salt content in aqueous solutions.

2. Experimental section

2.1. Materials and measurements

The reagents and materials used in this paper were all purchased

https://doi.org/10.1016/j.ica.2021.120344

Received 11 January 2021; Received in revised form 5 March 2021; Accepted 5 March 2021 Available online 13 March 2021 0020-1693/© 2021 Published by Elsevier B.V.



^{*} Corresponding author. E-mail address: dongwk@126.com (W.-K. Dong).



Scheme 1. Synthetic route to PNS.

commercially and can be used directly without further purification. The melting points of the compounds were measured using SGW X-4A Shanghai Jingke Slight Melting Point Instrument (Shanghai, China). The ¹H NMR spectra were measured by an AVANCE DRX-400 / 500 spectrometer using CDCl₃ as solvent (Bruke, Germany). C, H and N analyses were performed via a GmbH VarioEL V3.00 automatic elemental analyser (Berlin, Germany). Elemental analyses for metal(II) were conducted using an IRIS ER/S·WP – 1 ICP atomic emission spectrometer (Berlin, Germany). The fluorescence spectra of the probe **PNS** and the **PNS-Cu** complex were measured by an F-7000 FL 220–240 V spectrophotometer (Tokyo, Japan). X-ray single crystal structure determination was carried out on SuperNova, Dual (Cu at zero) AtlasS2 four-circle diffractometer.

2.2. The synthetic route to probe PNS

The synthetic route to sensor **PNS** is presented in Scheme 1. First, 1,2-dibromoethane (3.35 mL, 25.3 mmol) was added to the DMF solution containing *N*-hydroxyphthalimide (8.10 g, 50.5 mmol) and stirred thoroughly to obtain A1. An excess of hydrazine hydrate was added to the ethanol solution of A1 under nitrogen-protected conditions and stirred for 24 h to obtain A2. Then, 2-hydroxy-1-naphthaldehyde (172 mg, 1 mmol) was added drop by drop to the ethanol solution containing A2 (92.1 mg, 1 mmol) and reacted at 55 °C for 6 h to obtain N1. Finally, 2-formylpyridine (107 mg, 1 mmol) was slowly added to the ethanol solution (20.0 mL) of N1 (246 mg, 1 mmol). The mixed solution was reacted at 55 °C for 4 h. After purified by column chromatography, the crude product was purified (petroleum ether:ethyl acetate = 6:1) to obtain a white crystalline solid of sensor **PNS** 226 mg. Yield: 67.4%. M. p.: 72–74 °C. Anal. Calc. for C₁₉H₁₇N₃O₃: C, 68.05; H, 5.11; N, 12.38%. found: C, 68.24; H, 5.03; N, 12.57%.

2.3. The preparation of sensor PNS-Cu solution

Weighing the sensor **PNS** (10.7 mg, 0.10 mmol) and Cu(NO₃)₂ (18.7 mg, 0.10 mmol), and then dissolving them in 10 mL DMSO solution, stirred at 50 °C for 20 min. After cooling to room temperature, the solution was diluted to 1×10^{-5} M and set aside.

2.4. Stock solution preparation for spectral detection

The cations of all anionic tested salts are Na⁺ and the anions of all metal salts used in all experiments are NO₃⁻. Stock solutions of the 16 metal nitrates (Cd²⁺, Cr³⁺, Ag⁺, Pb²⁺, Na⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Mg²⁺, Fe³⁺, Al³⁺, Li⁺, Ca²⁺, K⁺, and Mn²⁺) and the 16 sodium salts (H₂PO₄⁻, NO₃⁻, I⁻, HS⁻, Br⁻, F⁻, SCN⁻, Cl⁻, AcO⁻, NO₂⁻, HCO₃⁻, HPO₄²⁻, ClO₄⁻, N₃⁻, CN⁻ and S²⁻) were prepared in double distilled water at a concentration of 1 \times 10⁻⁴ M. The sensors (**PNS** and **PNS-Cu**) are



Fig. 1. Fluorescence Intensity of PNS in DMSO solution at different water content conditions. ($\lambda_{ex}=301$ nm, $\lambda_{em}=400$ nm).

dissolved in DMSO:H₂O = 9:1 at a concentration of 1×10^{-5} M.

2.5. Solution selection for sensor PNS

Salamo-based ligand contains two electronegative oxygen atoms on the basis of Salen-based ligand, its stability is significantly improved, and overcomes the shortcomings of the easy hydrolysis of Salen-based ligand. Previous studies have shown that Salamo-based fluorescent probes do not hydrolyze in aqueous systems [2]. The sensor molecule **PNS** has good solubility in methanol, ethanol, dichloromethane, trichloromethane, acetonitrile, DMF and DMSO, but it has the strongest excitation luminescence in DMSO, so DMSO was chosen as the liquid environment for the sensor molecule. From Fig. 1, it can be concluded that the water content in the solution increases, the fluorescence intensity of the sensor molecule in solution gradually decreases. The sensor has stronger fluorescence when the water content was less than 40%, and the fluorescence tends to be constant when the water content reached 50%. Therefore, a 9:1 solution of DMSO:H₂O was selected to test the sensor performance.

3. Results and discussion

3.1. The response of Cu^{2+} to sensor **PNS**

3.1.1. Fluorescence recognition of Cu^{2+}

The fluorescence spectra of the sensor **PNS** to Cu^{2+} were measured in an DMSO:H₂O (9:1 v/v) solution, so the final concentration of the probe



Fig. 2. Fluorescence emission spectra of PNS (1 \times 10⁻⁵ M) in the absence and existence of different metal ions (1 \times 10⁻⁴ M) (Cd²⁺, Cr³⁺, Ag⁺, Pb²⁺, Na⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Mg²⁺, Fe³⁺, Al³⁺, Li⁺, Ca²⁺, K⁺, and Mn²⁺). (DMSO: H₂O = 9:1, λ_{ex} = 301 nm, λ_{em} = 400 nm).



Fig. 3. Fluorescence emission spectra of sensor **PNS** (1×10^{-5} M) with adding Cu²⁺ (0 ~ 1.0 equiv.). Inset: Naked eye identification of sensor **PNS** solution before and after increase of Cu²⁺ (1 equiv.).

was 1×10^{-5} M. As shown in Fig. 2, at an excitation wavelength of 301 nm, the sensor **PNS** possessed a fluorescence peak at about 400 nm. When 10 equivalents of metal ions were added to 1 equivalents of **PNS**, it was found that the characteristic peak of the sensor **PNS** at 400 nm disappear after the addition of Cu²⁺ ions. The sensor **PNS** performs very well in anti-interference experiment against Cu²⁺ ions, and therefore has the specificity to recognize Cu²⁺ ions. The titration experiment of Cu²⁺ ions on sensor **PNS** in Fig. 3 showed that when an equivalent amount of Cu²⁺ ions was added to the solution, the fluorescence intensity of the



Fig. 5. Comparison of emission wavelengths at 400 nm for 16 cation fluorescence intensities at 301 nm excitation wavelength. (1 \sim 16 = Ag⁺, Al³⁺, Ca²⁺, Cd²⁺, Co²⁺, Cr³⁺, Fe³⁺, Zn²⁺, K⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺, Mg²⁺, Li⁺ and Cu²⁺).

solution no longer changed significantly, thus it can be seen that sensor **PNS** forms a stable **PNS-Cu** complex in the form of 1:1 with Cu²⁺ ions in solution. In addition, an extremely good linear correlation (R² = 0.9013) was obtained between the fluorescence intensity at 400 nm and the Cu²⁺ ion concentration in the range of 0 ~ 0.5 equivalents. The detection limit of probe **PNS** for Cu²⁺ was then calculated to be 1.21×10^{-8} M based on the slope of the standard curve. These results indicate that sensor **PNS** can be used to qualitatively monitor Cu²⁺. The complexes formed by Cu²⁺ ions and sensor **PNS** are very stable, and only S²⁻ ions are known to displace Cu²⁺ ions from sensor **PNS**, so the recognition of Cu²⁺ ions by sensor **PNS** can be considered as an irreversible process without the involvement of S²⁻ ions.

3.1.2. Naked eye recognition of sensor **PNS** to Cu^{2+}

As can be seen in Fig. 4(a), after the addition of various metal ions to sensor **PNS**, only the Cu^{2+} ions can change the solution colour from colourless to a distinctly bright yellow upon addition. Under the 365 nm excitation light source, the Cu^{2+} ions can also change the sensor **PNS** solution colour significantly, which changes the solution colour from purple to dark, as shown in Fig. 4(b). Thus, it can be determined that the sensor **PNS** has specific recognition of Cu^{2+} ions at excitation wavelengths of 301, 365 nm and sunlight.

3.1.3. Selectivity of sensor **PNS** to Cu^{2+}

To evaluate the selectivity of sensor **PNS** for Cu^{2+} ions, we have verified the competition of various cations $(Cd^{2+}, Cr^{3+}, Ag^+, Pb^{2+}, Na^+, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Li^+, Ca^{2+}, K^+, and Mn^{2+})$ with Cu^{2+} ions in sensor **PNS**. The measurements were also repeated three times to take the average value for analysis. From the cation competition experiments in Fig. 5, it is evident that the sensor **PNS** has good identification properties for Cu^{2+} ions and no interference from other cations, thus, sensor **PNS** has specific discrimination for Cu^{2+} ions.



Fig. 4. a) Colors of sensor PNS (1×10^{-5} M) upon addition of various metal ions. b) Fluorescence emission of sensor PNS (1×10^{-5} M) upon addition of various metal ions. (no ion, Cd²⁺, Cr³⁺, Ag⁺, Pb²⁺, Na⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Mg²⁺, Fe³⁺, Al³⁺, Li⁺, Ca²⁺, K⁺, and Mn²⁺). (DMSO:H₂O = 9:1, $\lambda_{ex} = 365$ nm).

Table 1

Crystal data and structure parameters for PNS-Cu.

The Cu(II) complex	PNS-Cu		
Empirical formula	C19H16CuN4O6		
Formula weight	242.86		
T (K)	100.00(11)		
Wavelength (Å)	0.71073		
Crystal system	Triclinic		
Space group	P-1		
a (Å)	8.8614(4)		
b (Å)	16.9853(8)		
c (Å)	18.3238(9)		
α (°)	75.342(4)		
β (°)	89.162(4)		
γ (°)	89.238(4)		
V (Å ³)	2667.8(2)		
Ζ	12		
$D_{\text{calc}} (g \cdot \text{cm}^{-3})$	1.684		
F (000)	1481		
Crystal size (mm)	0.11 imes 0.1 imes 0.08		
θ Range (°)	2.4490 to 26.9200		
Index ranges	$-11 \leq h \leq 12$		
Index ranges Reflections collected/unique	$-23 \leq k \leq 20$		
	$-23 \leq l \leq 19$		
	12,451 / 7666 [R _{int} = 0.0591]		
Completeness to θ	99.42% ($\theta = 26.32$)		
Data/restraints/parameters	12,451 / 0 / 811		
GOF	1.017		
Final R_1 , w R_2 indices	0.0635, 0.1040		
R_1 , w R_2 indices (all data)	0.1165, 0.1291		
Largest diff. peak and hole	0.683 and –0.792 e.Å ^{–3}		

3.1.4. Crystals structure

Single-crystal X-ray diffraction determination showed that the **PNS-Cu** complex belongs to the triclinic crystal system with the space group P -1, which is described in Table 1. As shown in Fig. 6a and Table 1, the **PNS-Cu** complex was found to be an asymmetric Cu(II) complex consisting of one Cu(II) atom and one completely deprotonated ligand (L)⁻ unit. In the structure of the **PNS-Cu** complex, the nitrate anion is involved in the coordination. The five coordinated Cu(II) atom is located in the N₃O cavity of the fully deprotonated ligand (L)⁻ unit, using a slightly distorted tetragonal cone geometry, as shown in Fig. 6b, which shows the coordination polyhedron of the Cu(II) atom in the Cu(II) complex. The attainment of this single crystal also verifies the correctness of sensor **PNS** and sensor **PNS-Cu** recognition mechanism in this paper.

3.2. The response of S^{2-} to sensor **PNS-Cu**

3.2.1. Fluorescence recognition of S^{2-}

The fluorescence properties of the sensor **PNS-Cu** $(1 \times 10^{-5} \text{ M})$ were tested at DMSO:H₂O = 9:1. As shown in Fig. 7, the free sensor **PNS-Cu** has no fluorescence emission peak at 400–600 nm, a relatively small fluorescence peak appears at 400 nm when other anions (10 equivalents) were added, and a strong cyan-blue fluorescence peak appears at



Fig. 7. Fluorescence emission spectra of PNS-Cu solution $(1\times10^{-5} \text{ M})$ in the absence and existence of different anions $(1\times10^{-4} \text{ M})$ $(H_2PO_4^-, NO_3^-, I^-, HS^-, Br^-, F^-, SCN^-, Cl^-, AcO^-, NO_2^-, HCO_3^-, HPO_4^{--}, ClO_4^-, N_3^-, CN^- and S^{2-}).$ (DMSO:H₂O = 9:1, λ_{ex} = 301 nm, λ_{em} = 475 nm).

about 475 nm after S^{2-} (10 equivalents) was added.

To evaluate the sensitivity of **PNS-Cu** to S^{2-} , we investigated the titration experiment of **PNS-Cu** to S^{2-} and recorded the changes of the fluorescence spectra in this experiment. As shown in Fig. 8a, with increasing S^{2-} concentration, a brief fluorescence peak at about 400 nm first appeared, followed by a gradual decrease, and the fluorescence



Fig. 8. a) Fluorescence emission spectra of sensor PNS-Cu (1 \times 10⁻⁵ M) with adding S²⁻ (0 \sim 1.5 equiv.). Inset: Naked eye identification of sensor PNS solution before and after increase of S²⁻ (1.5 equiv.). b) Fluorescence intensity at 475 nm with S²⁻ ion titration curve. (λ_{ex} = 301 nm).



Fig. 6. a) Crystal structure of PNS-Cu. b) Coordination environment for Cu(II) atom.



Fig. 9. Comparison of 16 anion fluorescence intensities at 475 nm emission wavelength at 301 nm excitation wavelength. $(1 \sim 16 = H_2PO_4^-, AcO^-, Br^-, Cl^-, ClO_4^-, CN^-, F^-, HPO_4^{2-}, HS^-, I^-, N_3^-, NO_3^-, NO_2^-, SCN^-, HCO_3^-, and S^{2-}).$

intensity at 475 nm gradually increased (Fig. 8a) and stabilized after 1.5 eq. Moreover, an excellent linear relationship (R² = 0.9672) was also obtained between the fluorescence intensity at 475 nm and the S²⁻ concentration in the range of 0 ~ 1.5 equivalents (Fig. 8b). Finally, the binding constant K for **PNS-Cu** and S²⁻ was estimated to be 1.79 × 10⁶ M^{-1} by the Scatchard equation, and the result indicates that the reaction of **PNS-Cu** and S²⁻ has a particularly high stability. The detection limit of **PNS-Cu** for S²⁻ was then calculated to be 5.58 × 10⁻⁹ M based on the slope of the standard curve. These results indicate that **PNS-Cu** can qualitatively monitor S²⁻ and then further optimized.

In this way, the maximum emission wavelength is red-shifted, which indicates that no new bonds are formed between **PNS-Cu** and S^{2-} during the bonding process. It is speculated that the fluorescence change may be due to a simple displacement reaction process and the formation of stable compounds of CuS after ion exchange.



Fig. 11. Fluorescence intensities measured at different pH values.

3.2.2. Selectivity of sensor **PNS-Cu** to S^{2-}

To evaluate the selectivity of sensor **PNS-Cu** for S^{2-} ions, we have verified the competition of various anions (H₂PO₄⁻, NO₃⁻, I⁻, HS⁻, Br⁻, F⁻, SCN⁻, Cl⁻, AcO⁻, NO₂⁻, HCO₃⁻, HPO₄²⁻, ClO₄⁻, N₃⁻, CN⁻ and S²⁻) with S²⁻ ions in sensor **PNS-Cu**. The measurements were also repeated three times to take the average value for analysis. In the competitive experiment, it was found that the fluorescence enhancement was relatively weak after the addition of a few anions to the solution containing S²⁻, which might be caused by the change of the solution fluorescence due to the decrease of the solution concentration after the addition of other anions, but the fluorescence intensity of the solution was still significantly enhanced.

In the anion competition experiments of Fig. 9, other anions also did not significantly interfere with S^{2-} ions, so sensor **PNS-Cu** has specific recognition of S^{2-} .



Fig. 10. Density functional theory (DFT) calculations of sensor PNS, PNS-Cu, and fluorescent molecule PNS⁻. Left: PNS; Medium: PNS-Cu; Right: PNS⁻.

Table 2

Compa

System	Signal output	Linear range (µM)	LOD (M)	References
	Colorimetry	0–20	1.02×10^{-6}	[16a]
	Fluorescence	0–20	2.05×10^{-7}	[18]
	Fluorescence	0–5	$2.67 imes 10^{-8}$	[2b]
	Fluorescence	0–10	$3.27 imes 10^{-8}$	[23]
	Fluorescence	0–15	1.52×10^{-8}	[24]
	Fluorescence	0–10	4.47×10^{-7}	[25]
	Colorimetry	0–5	2.81×10^{-8}	[26]
HÓ Ph Ph H N N N H N N H N N H	Colorimetry	0400	$1.5 imes 10^{-7}$	[27]
	Colorimetry	0–20	2.26×10^{-6}	[28]
PNS	Fluorescence	0–5	$1.21 imes 10^{-8}$	This work

Table 3

Comparison of different sensors for S^{2-} detection.

1				
System	Signal output	Linear range (µM)	LOD (M)	References
ABTS-Au (III) system	Colorimetry	0.5–15	$2.8 imes 10^{-7}$	[19]
	Colorimetry	0–3.5	5.7×10^{-9}	[20]
S N N OH				
Bare Au nanoparticles colorimetry	Colorimetry	0.5–10	$8 imes 10^{-8}$	[21]
CDs/PEI/NB/Cu ²⁺	Fluorescence	0.1-8.0	6×10^{-8}	[22]
	Fillorescence	0-7.5	1.2 × 10	נסח
	Fluorescence	0–15	1.79×10^{-8}	[24]
	Fluorescence	0–10	9.12×10^{-7}	[25]
	Colorimetry	1.5–90	3.35×10^{-7}	[29]
PNS-Cu	Fluorescence	0–15	5.58×10^{-9}	This work

3.3. The sensing mechanism of sensor **PNS-Cu** to S^{2-}

In order to further understand the reaction mechanism of these two sensors, we analyzed the ion state in the solution under different conditions during continuous sensing by mass spectrometry. We know from the mass spectrometry under different conditions that when sensor **PNS** detects Cu^{2+} ions in the solution, the free copper(II) ions in the solution combine with sensor **PNS** to form a new complex, which quenched the fluorescence of the **PNS** solution that originally emits fluorescence, as shown in Figs. S2 and S3. During the detection of the anions by sensor **PNS-Cu**, the free S²⁻ ions in the solution combine with the copper(II) ions in the sensor, and the original copper(II) ions in the sensor were quenched by the fluorescence. The position of the ion is occupied by the Na⁺ ion in the solution, and the solution resumes fluorescence, as shown in Figure S3.

3.4. DFT-theoretical analysis of the sensing mechanism

The electron distributions of **PNS** and **PNS-Cu** before and after sensing with the target ions by Gaussian 09 program density functional theory (DFT) [17]. Density functional theory (DFT) calculations showed that the HOMO-LUMO orbital electron clouds of sensor **PNS** are distributed on the side of the naphthalene ring of the luminescent group of the molecule, and after binding with Cu^{2+} ion, the HOMO-LUMO orbital electron clouds are shifted towards Cu^{2+} and pyridine. When the S^{2-} ion snatches the Cu^{2+} ion from the sensor **PNS-Cu**, the HOMO orbital electron cloud of the molecule is shifted back to the luminescence group, thus making the solution fluorescent again. In addition, the energy LUMO (-2.067 eV) is lower than that of the fluorophore LUMO (-1.512 eV) in the sensor **PNS** due to the calculated energy in the **PNS**- Cu complex. More importantly, the HOMO-LUMO energy gap before and after the interaction of sensor PNS with Cu²⁺ also decreased from 4.041 eV to 2.418 eV. in other words, the combination of Cu^{2+} and sensor **PNS** made the system more stable. Thus, we speculate that the fluorescence quenching mechanism of the interaction between sensor PNS and Cu²⁺ ions is photo-induced electron transfer (PET), as shown in Fig. 10. Before the binding of sensor and Cu^{2+} ions, when the sensor was transferred from the fundamental state to the excited state via the excited light source, no significant electron transfer occurred and there was no significant change in fluorescence. However, after the combination of **PNS** and Cu²⁺ ions, the excited state electrons on the **PNS-Cu** complex were transferred to the Cu^{2+} ions, so that the excited state electrons on the PNS-Cu complex could not return to the ground state, and fluorescence quenching occurred. After the introduction of sodium sulfide, the copper(II) element in the complex combined with S^{2-} to form a copper(II) sulfide precipitate, and the electron transfer process, which was originally blocked, was reopened, so that fluorescence appeared again. The calculated results are just in agreement with the speculated mechanism.

3.5. Effect of pH

In practical applications, the sensor also needs to be applied to physiological pH, so we measured the fluorescence intensity at different pH values after adding Cu^{2+} and S^{2-} to **PNS**, respectively, as shown in Fig. 11. It was found that the fluorescence intensity of the **PNS** solution is weak in the pH range of 2 ~ 3, which can be attributed to negligible deactivation in strongly acidic solutions, and is significantly enhanced between 4 and 11. PNS can be said to be relatively stable in this range. **PNS-Cu** solutions are also suitable between 3 and 11. The pH values

measured after the addition of S^{2-} to the **PNS-Cu** solution showed slight fluctuations between 4 and 11 and showed a strong fluorescence intensity in this range. After pH = 12, it is not discussed further as the solution's alkaline test molecule's luminescence is enhanced and not easily detected. **PNS** was found to be stable for the detection of Cu^{2+} and S^{2-} in the pH range of $4 \sim 11$. This solution can be used as an excellent chemical sensor.

3.6. Comparison between PNS and other probes

From Table 2, it can be observed that among the four Cu^{2+} fluorescence probes, sensor **PNS** has a lower detection limit for recognizing copper(II) ions than the relative sensors in other articles [2b,6b,18]. Also, in Table 3, sensor **PNS-Cu** has improved sensitivity to S²⁻ compared to the other four S²⁻ probes [19–22]. It is thus clear that sensor **PNS** and **PNS-Cu** are more sensitive than the other relative sensors in the above table.

4. Conclusion

A novel half-salomo-based chemical sensor **PNS** was synthesized firstly, and can continuously recognize Cu^{2+} and S^{2-} ions in solution. Sensor **PNS** has a high binding constant to Cu^{2+} ions and a detection limit of 1.21×10^{-8} M, and can recognize Cu^{2+} ions with the naked eye under both 301 and 365 nm excitation light sources. The new sensor **PNS-Cu** combined by **PNS** with Cu^{2+} ions can further recognize S^{2-} ions in solution and has a lower detection limit of 5.58×10^{-9} M. It has also been demonstrated that the half-salomo-based complex chemical sensor, which are derived from the half-ssalomo-based sensor **PNS**, can also be used to detect ions in aqueous solutions.

CRediT authorship contribution statement

Wen-Ze Zhang: Data curation, Formal analysis, Investigation, Methodology, Project administration, Writing - original draft. Ruo-Yu Li: Data curation, Formal analysis, Investigation, Methodology. Peng Li: Project administration, Software. Zhuang-Zhuang Chen: Formal analysis, Investigation. Wen-Kui Dong: Project administration, Conceptualization, Funding acquisition, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science findation of China (21761018) and the Program for Excellent Team of Scientific Research in Lanzhou Jiaotong University (201706), both of which are gratefully acknowledged.

Declaration of Competing Interest

There are no conflicts of interest to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120344.

References

[1] S. Lutsenko, Curr. Opin. Chem. Bio. 14 (2010) 211-217.

- [2] (a) J.Y. Uriu-Adams, C.L. Keen, Mol. Aspects. Med. 26 (2005) 268–298;
 (b) L. Wang, Z.L. Wei, C. Liu, W.K. Dong, J.X. Ru, Spectrochim. Acta A 239 (2020), 118496.
- [3] B.B. Tewari, J. Chem. Eng. Data 55 (2010) 1779–1783.
- [4] (a) P.A. Gale, C. Caltagirone, Coordin. Chem. Rev. 354 (2018) 2–27;
 (b) L. Tang, P. Zhou, Q. Zhang, Z. Huang, J. Zhao, M. Cai, Inorg. Chem. Commun. 36 (2013) 100–104;
 - (c) A. Mohammadi, J. Jabbari, J. Enviro. Chem. Eng. 94 (2016) 631-636;
 - (d) A. Mohammadi, M. Kianfar, J. Photochem. Photobio. A 367 (2018) 22-31;
 - (e) F.S. Zabihi, A. Mohammadi, Spectrochim. Acta A 238 (2020), 118439;
 (f) M. Yu, H.R. Mu, L.Z. Liu, N. Li, Y. Bai, X.Y. Dong, Chin. J. Inorg. Chem. 35 (2019) 1109–1120.
- [5] (a) N. Paul, R. Sarkar, R. Sarkar, A. Barui, S. Sarkar, J. Chem. Enc. 132 (2020) 21;
 (b) A. Paul, S. Anbu, G. Sharma, M.L. Kuznetsov, M.F.C.G.D. Silva, B. Kochb, A.J. L. Pombeiro, Dalton Trans. 44 (2015) 16953–16964;

(c) O. Choi, T.E. Clevenger, B. Deng, R.Y. Surampalli, L. Ross Jr, Z. Hu, Water Res. 43 (2009) 1879–1886;

(d) D.Y. Park, K.Y. Ryu, J.A. Kim, S.Y. Kim, C. Kim, Tetrahedron 72 (2016) 3930–3938;

- (e) C.S. Kwan, T. Wang, S.M. Chan, Z.W. Cai, K.C.F. Leung, Dalton Trans. 538 (2020) 528-532;
- (f) X.J. Yan, Z.G. Wang, Y. Wang, Y.Y. Huang, H.B. Liu, C.Z. Xie, Q.Z. Li, J.Y. Xu, Spectrochim. Acta A 243 (2020), 118797;
- (g) X.X. An, Z.Z. Chen, H.R. Mu, L. Zhao, Inorg. Chim. Acta 511 (2020), 119823.
 [6] (a) Y. Feng, Y. Yang, Y.Z. Wang, F.Z. Qiu, X.R. Song, X.L. Tang, G.L. Zhang, W.
- S. Liu, Sens. Actuators B 288 (2019) 27–37;
 (b) J.F. Wang, T. Feng, Y.J. Li, Y.X. Sun, W.K. Dong, Y.J. Ding, J. Mol. Struct. 1231 (2021), 129950;
- (c) L. Xu, M. Yu, L.H. Li, J.C. Ma, W.K. Dong, J. Struct. Chem. 60 (2019) 1358–1365.
- [7] (a) Z.L. Wei, L. Wang, J.F. Wang, W.T. Guo, Y. Zhang, W.K. Dong, Spectrochim. Acta A 228 (2020), 117775;
 - (b) Y. Zhang, L.Z. Liu, Y.D. Peng, N. Li, W.K. Dong, Transit. Metal. Chem. 44 (2019) 627-639;
 - (2019) 627–639;
 (c) R.N. Bian, J.F. Wang, Y.J. Li, Y. Zhang, W.K. Dong, J. Photochem. Photobio. A 400 (2020), 112719;

(d) Z.L. Wei, L. Wang, S.Z. Guo, Y. Zhang, W.K. Dong, RSC Adv. 9 (2019) 41298-41304:

- (e) H.R. Mu, X.X. An, C. Liu, Y. Zhang, W.K. Dong, J. Struct. Chem. 61 (2020) 1155–1166:
- (f) X. Xu, F. Tao, S.S. Feng, W.K. Dong, Appl. Organomet. Chem. 35 (2021), e6057.
- [8] (a) Q.P. Kang, X.Y. Li, Z.L. Wei, Y. Zhang, W.K. Dong, Polyhedron 165 (2019) 38–50;

(b) X.Y. Li, Q.P. Kang, C. Liu, Y. Zhang, W.K. Dong, New J. Chem. 43 (2019) 4605–4619;

- (c) X.X. An, Q. Zhao, H.R. Mu, W.K. Dong, Crystals 9 (2019) 101;
- (d) Q. Zhao, X.X. An, L.Z. Liu, W.K. Dong, Inorg. Chim. Acta 490 (2019) 6-15;
- (e) S.Z. Guo, Y.J. Lia, S.S. Feng, W.K. Dong, Russ. J. Gen. Chem. 90 (2020) 1–9.
- [9] L.Q. Chai, L.J. Tang, L.C. Chen, J.J. Huang, Polyhedron 122 (2017) 228–240.
 [10] (a) X.X. An, C. Liu, Z.Z. Chen, K.F. Xie, W.K. Dong, Crystals 9 (2019) 602;
- [10] (a) X.X. An, C. Liu, Z.Z. Chen, K.F. Ale, W.K. Dong, Crystals 9 (2019) 602;
 (b) Y.F. Cui, Y. Zhang, K.F. Xie, W.K. Dong, Crystals 9 (2019) 596;
 (c) Y. Zhang, Y.Q. Pan, M. Yu, X. Xu, W.K. Dong, Appl. Organomet. Chem. 33 (2019), e5240;
 (d) P. Li, G.X. Yao, M. Li, W.K. Dong, Polyhedron 195 (2021), 114981;
 (e) J.F. Wang, X. Xu, R.N. Bian, W.K. Dong, Y.J. Ding, Inorg. Chim. Acta 516
- (2021), 120095.
 [11] (a) Y. Zhang, M. Yu, Y.Q. Pan, Y. Zhang, L. Xu, X.Y. Dong, Appl. Organomet. Chem. 34 (2020), e5442:
 - (b) L.W. Zhang, Y. Zhang, Y.F. Cui, M. Yu, W.K. Dong, Inorg. Chim. Acta 506 (2020), 119534.
- [12] (a) Y.Q. Pan, Y. Zhang, M. Yu, Y. Zhang, L. Wang, Appl. Organomet. Chem. 34 (2020), e5441;
 - (b) L. Wang, Z.L. Wei, Y.Q. Pan, Y. Zhang, W.K. Dong, Chin. J. Inorg. Chem. 35 (2019) 1791–1804;
 - (c) L.Z. Liu, M. Yu, X.Y. Li, Q.P. Kang, W.K. Dong, Chin. J. Inorg. Chem. 35 (2019) 1283–1294;
 - (d) S.Z. Zhang, J. Chang, H.J. Zhang, Y.X. Sun, Y. Wu, Y.B. Wang, Chin. J. Inorg. Chem. 36 (2020) 503–514;
 - (e) J. Li, H.J. Zhang, J. Chang, Y.X. Sun, Y.Q. Huang, Crystals 8 (2018) 176;
 (f) H.J. Zhang, J. Chang, H.R. Jia, Y.X. Sun, Chin. J. Inorg. Chem. 34 (2018) 2261–2270;
 - (g) J. Chang, H.J. Zhang, H.R. Jia, Y.X. Sun, Chin. J. Inorg. Chem. 34 (2018) 2097–2107;
 - (h) H.R. Jia, J. Chang, H.J. Zhang, J. Li, Y.X. Sun, Crystals 8 (2018) 272.
- [13] (a) L. Wang, Z.L. Wei, Z.Z. Chen, C. Liu, W.K. Dong, Y.J. Ding, Microchem. 155 (2020), 119823;
- (b) R.N. Bian, J.F. Wang, X. Xu, X.Y. Dong, Y.J. Ding, Appl. Organomet. Chem. 35 (2021), e6040.
- [14] (a) M. Yu, Y. Zhang, Y.Q. Pan, L. Wang, Inorg. Chim. Acta 509 (2020), 119701;
 (b) Y.X. Sun, Y.Q. Pan, X. Xu, Y. Zhang, Crystals 9 (2019) 607;
 (c) L. Wang, Z.L. Wei, Z.Z. Chen, C. Liu, W.K. Dong, Microchem. 155 (2020), 104801;
 - (d) C. Liu, Z.L. Wei, H.R. Mu, W.K. Dong, Y.J. Ding, J. Photochem. Photobio. A 397 (2020), 112569:
 - (e) R.N. Bian, J.F. Wang, Y.J. Li, Y. Zhang, W.K. Dong, J. Photochem. Photobiol. A 400 (2020), 112829;

W.-Z. Zhang et al.

(f) X. Xu, R.N. Bian, S.Z. Guo, W.K. Dong, Y.J. Ding, Inorg. Chim. Acta 513 (2020), 119945.

- [15] (a) Q.P. Kang, X.Y. Li, L. Wang, Y. Zhang, W.K. Dong, Appl. Organomet. Chem. 33 (2019), e5013;
 - (b) L.Z. Liu, L. Wang, M. Yu, Q. Zhao, Y. Zhang, Y.X. Sun, W.K. Dong, Spectrochim. Acta A 222 (2019), 117209.
- [16] (a) Y.Q. Pan, X. Xu, Y. Zhang, Y. Zhang, W.K. Dong, Spectrochim. Acta A 229 (2020), 117927;
 - (b) H.R. Mu, M. Yu, L. Wang, Y. Zhang, Y.J. Ding, Phosphorus Sulfide Silicon Relat. Elem. 195 (2020) 730–739;
 - (c) R.N. Bian, X. Xu, T. Feng, W.K. Dong, Inorg. Chim. Acta 516 (2021), 120098;
 (d) J.F. Wang, R.N. Bian, T. Feng, K.F. Xie, L. Wang, Y.J. Ding, Microchem. J. 160 (2021), 105676;
 - (e) R.Y. Li, Z.L. Wei, L. Wang, Y. Zhang, J.X. Ru, Microchem. J. 162 (2021), 105720;
 - (f) Y.F. Cui, C. Liu, Y. Zhang, Y. Zhang, Inorg. Nano-Met. Chem. 51 (2021) 288–295;
 - (g) Y.D. Peng, R.Y. Li, P. Li, Y.X. Sun, Crystals 11 (2021) 113.
- [17] (a) C. Liu, X.X. An, Y.F. Cui, K.F. Xie, W.K. Dong, Appl. Organomet. Chem. 34 (2020), e5272;
 - (b) J. Chang, S.Z. Zhang, Y. Wu, H.J. Zhang, Y.X. Sun, Transit. Metal Chem. 45 (2020) 279–293;
 - (c) K.F. Xie, J.C. Xu, P. Liu, Appl. Surf. Sci. 461 (2018) 175-181;
 - (d) K.F. Xie, P. Liu, J.F. Zhang, X.J. Li, L. Fu, Mater. Today Commun. 24 (2020), 101322;

(e) J.F. Wang, R.Y. Li, P. Li, W.K. Dong, Inorg. Chim. Acta 518 (2021), 120247;
(f) Y.J. Li, S.Z. Guo, T. Feng, K.F. Xie, W.K. Dong, J. Mol. Struct. 1228 (2021), 129796;

- (g) T. Feng, L.L. Li, Y.J. Li, W.K. Dong, Acta Cryst. B 77 (2021) 168–181.
 [18] (a) W.K. Dong, X.L. Lia, L. Wang, Y. Zhang, Sens. Actuators B 229 (2016) 370–378;
- (b) X. Xu, Y.J. Li, T. Feng, W.K. Dong, Y.J. Ding, Luminescence 36 (2021) 169–179.
- [19] C. Chen, D. Zhao, L. Lu, F. Yang, X. Yang, Sens. Actuators B 220 (2015) 1247–1253.
- [20] F.S. Zabihi, A. Mohammadi, Spectrochim. Acta A 238 (2020), 118439.
 [21] H.H. Deng, S.H. Weng, S.L. Huang, L.N. Zhang, A.L. Liu, X.H. Lin, W. Chen, Anal. Chim. Acta 852 (2014) 218–222.
- [22] H. Jin, R. Gui, Y. Wang, J. Sun, Talanta 169 (2017) 141-148.
- [23] Z.Y. Zuo, Y.P. Tang, F.H. Lei, R.Y. Jin, P.C. Yin, Y. Li, Q.F. Niu, Sens. Actuators B 242 (2020), 118712.
- [24] X.J. Yan, Z.G. Wang, Y. Wang, Y.Y. Huang, H.B. Liu, C.Z. Xie, Q.Z. Li, J.Y. Xu, Spectrochim. Acta A 243 (2020), 118797.
- [25] L.J. Tang, X. Dai, M.J. Cai, J. Zhao, P. Zhou, Z.L. Huang, Spectrochim. Acta A 122 (2014) 656–660.
- [26] Z.G. Guo, Q.F. Niu, T.D. Li, T. Sun, H. Chi, Spectrochim. Acta A 213 (2019) 97–103.
- [27] R. Chandra, A. Ghorai, G.K. Patra, Sens. Actuators B 255 (2018) 701-711.
- [28] A.K. Manna, J. Mondal, K. Rout, G.K. Patra, Sens. Actuators B 275 (2018) 350-358.
- [29] A.K. Manna, J. Mondal, R. Chandra, K. Rout, G.K. Patra, Anal. Methods 10 (2018) 2317–2326.